LUMINESCÊNCIA DE A-WILLEMITE NA OXIDAÇÃO CATALÍTICA DE MONÓXIDO DE CARBONO

LUMINESCENCE OF A-WILLEMITE IN THE CATALYTIC OXIDATION OF CARBON MONOXIDE

ЛЮМИНЕСЦЕНЦИЯ А-ВИЛЛЕМИТА ПРИ КАТАЛИТИЧЕСКОМ ОКИСЛЕНИИ МОНООКСИДА УГЛЕРОДА

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RESUMO

A interação de partículas neutras de gás de energias térmicas (moléculas e átomos) com a superfície do sólido é acompanhada por radiação nas partes visível e infravermelha do espectro. Nesse caso, a superfície do sólido atua como um catalisador para as reações de recombinação de partículas de gás. Neste contexto, é interessante a possibilidade de excitar a luminescência durante a oxidação catalítica do monóxido de carbono diretamente pela forma atômica de oxigênio pré-adsorvido na superfície do sólido. Os métodos cinéticos e espectrais foram utilizados para estudar a luminescência resultante da oxidação catalítica do monóxido de carbono pela forma atômica de oxigênio pré-adsorvido na superfície do sólido – uma amostra de α -willemite $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$. As principais etapas dos mecanismos de recombinação entre as partículas dos adsorbatos são estabelecidas. As transições eletrônicas em complexos de adsorção e no íon ativador foram identificadas. Durante o processo de entrada, a temperatura da amostra foi mantida pelo sistema de controle eletrônico de alta velocidade constante da corrente do aquecedor. Isso ajudou a evitar os efeitos térmicos colaterais. As principais etapas dos mecanismos de recombinação entre as partículas dos adsorbatos são estabelecidas. As transições eletrônicas em complexos de adsorção e no íon ativador foram identificadas. Verificou-se que a excitação da luminescência ocorre em duas etapas principais, um pouco deslocadas no tempo. O mecanismo de duas etapas da oxidação catalítica do monóxido de carbono na superfície da α -willemite pelo oxigênio atômico pré-adsorvido permite descrever consistentemente a luminescência observada neste caso. Este tipo de luminescência tem a perspectiva no estudo dos mecanismos de oxidação catalítica do monóxido de carbono.

Palavras-chave: cristalofósforo, α -willemite, monóxido de carbono, cinética de luminescência, espectro de luminescência.

ABSTRACT

The interaction of neutral gas particles of thermal energies (molecules and atoms) with the surface of a solid is accompanied by radiation in the visible and I.R. parts of the spectrum. In this case, the surface of a solid body acts as a catalyst for the recombination reactions of gas particles. In this connection, the possibility of exciting luminescence during the catalytic oxidation of carbon monoxide directly by the atomic form of oxygen pre-adsorbed on the surface of a solid is of interest. Kinetic and spectral methods were used to study the luminescence arising from the catalytic oxidation of carbon monoxide by the atomic form of oxygen pre-adsorbed on the surface of a solid – a sample of α -willemite $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$. The main stages in the mechanisms of recombination between adsorbate particles are established. Electronic transitions in adsorption complexes and the activator ion have been identified. During the filling process, the sample temperature was maintained by a constant high-speed electronic control system of the heater current. This made it possible to avoid thermal

side effects. The main stages in the mechanisms of recombination between adsorbate particles are established. Electronic transitions in adsorption complexes and the activator ion have been identified. It was found that luminescence excitation proceeds in two main stages, somewhat time-shifted. The two-stage mechanism for the catalytic oxidation of carbon monoxide on the surface of α -willemite with pre-adsorbed atomic oxygen allows a consistent description of the luminescence observed in this case. This type of luminescence has the prospect of using for studying the mechanisms of catalytic oxidation of carbon monoxide.

Keywords: *crystallophosphorus, α -willemite, carbon monoxide, luminescence kinetics, luminescence spectrum.*

АННОТАЦИЯ

Взаимодействие нейтральных газовых частиц тепловых энергий (молекул и атомов) с поверхностью твердого тела сопровождается излучением в видимой и инфракрасной частях спектра. При этом поверхность твердого тела выступает в роли катализатора реакций рекомбинации газовых частиц. В связи с этим вызывает интерес возможность возбуждения люминесценции при каталитическом окислении монооксида углерода непосредственно атомарной формой кислорода, преадсорбированной на поверхности твердого тела. Кинетическими и спектральными методами исследована люминесценция, возникающая при каталитическом окислении монооксида углерода атомарной формой кислорода, преадсорбированной на поверхности твердого тела – образца α -виллемита $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$. Установлены основные стадии в механизмах рекомбинации между частицами адсорбатов. Идентифицированы электронные переходы в адсорбционных комплексах и в ионе активатора. В процессе напуска температура образца поддерживалась постоянной быстродействующей электронной системой регулирования тока нагревателя. Это позволило избежать побочных тепловых эффектов. Установлены основные стадии в механизмах рекомбинации между частицами адсорбатов. Идентифицированы электронные переходы в адсорбционных комплексах и в ионе активатора. Было обнаружено, что возбуждение люминесценции происходит в два основных этапа, несколько смещенных во времени. Двухстадийный механизм каталитического окисления оксида углерода на поверхности α -виллемита предварительно адсорбированным атомарным кислородом позволяет последовательно описать люминесценцию, наблюдаемую в этом случае. Этот тип люминесценции имеет перспективу использования для изучения механизмов каталитического окисления оксида углерода.

Ключевые слова: *кристаллофосфор, α -виллемит, оксид углерода, кинетика люминесценции, спектр люминесценции.*

1. INTRODUCTION

The interaction of neutral gas particles of thermal energies (molecules and atoms) with the surface of a solid is accompanied by radiation in the visible and I.R. parts of the spectrum (Rufov *et al.*, 1966; Volkenstein *et al.*, 1976; Arnold and Coleman, 1988; Formalev *et al.*, 2019; Radyuk *et al.*, 2019). In this case, the surface of a solid body acts as a catalyst for the recombination reactions of gas particles. Claydel and his coworkers introduced the concept of cathodoluminescence (Breysse *et al.*, 1978) to denote the glow of a solid during a catalytic process on its surface. In particular, in (Breysse *et al.*, 1978; Lurie *et al.*, 2017), it is a question of chemiluminescence arising during the (Equation 1) catalytic process on the ThO_2 surface activated by rare-earth ions Pr^{3+} , Eu^{3+} , Dy^{3+} and Gd^{3+} . The interpretation of this type of luminescence is given in the model of the energy bands of a solid with allowance for the local levels induced on the surface by the adsorbate (Achatz *et al.*, 2011). Radiative transitions are supposed from the O^- level formed

by the dissociative charged form of molecular oxygen adsorption to the CO^+ level in the band gap and from the conduction band to the activator level.

In this connection, the possibility of exciting luminescence during the catalytic oxidation of carbon monoxide directly by the atomic form of oxygen pre-adsorbed on the surface of a solid and, thereby, obtaining more detailed information on the mechanism of catalytic oxidation of carbon monoxide is of interest (Kharisov and Kharissova, 2019). As an adsorbent, α -willemite $\text{Zn}_{1.98}\text{Mn}_{0.02}\text{SiO}_4$ was selected (sample FGI-520-1 of crystallophosphorus $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$, synthesized at the State Institute of Applied Chemistry, Russian Federation). Due to the high luminescence efficiency during cathodic and photoexcitation, chemical and thermal stability, this crystallophosphorus is widely used in optoelectronic technology and lighting devices (Juanjuan *et al.*, 2015; Ni *et al.*, 2018). The morphology, phase composition, and structure of the crystal lattice have been well studied for

$\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$, and the main electronic transitions in spectral laws have been determined (Palumbo and Brown, 1970; Stevels and Vink, 1974; Dove *et al.*, 1981; Hess and Krautz, 1981; Rivera-Enríquez *et al.*, 1981; Formalev *et al.*, 2018; Skvortsov *et al.*, 2014). In addition, $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ demonstrates a clear ability for radical recombination luminescence upon excitation by atomic gases (Rufov *et al.*, 1966; Barashkin and Samarin, 2005). All this leads to the choice of α -willemite as a sample for studying this type of luminescence in order to facilitate the interpretation of the kinetic and spectroscopic results of the experiment (Sarrigani and Amiri, 2019; Koshoridze *et al.*, 2017).

2. MATERIALS AND METHODS

The experiments were performed on a special high-vacuum installation, whose main components are given in (Shigalugov *et al.*, 2019). A dynamic vacuum of 10^{-8} Torr in the sample chamber was maintained by two magnetic discharge pumps NMD-04-1 and NMD-016-1 (with a total pumping rate of 550 l/s). High purity gases were used: oxygen puriss. spec. (99.998%) and carbon monoxide CO puriss. (99.9%). The luminescence intensity was recorded using photoelectric devices: a photomultiplier (FEM-84-3), the signal from which was fed through a preamplifier (C7319 HAMAMATSU) to a computer recording module (ML-840 PowerLab 4/20 ADInstruments), or (at low light fluxes) to a photosensor module (H7468-01 HAMAMATSU) docked with an IBM PC (Zhou *et al.*, 2015). Luminescence spectra in the region of 350-1150 nm with a resolution of 1.5 nm were recorded by a scanning CCD array spectrograph (QE 65000 OCEAN OPTICS), also controlled by P.C. The temperature of a finely dispersed sample deposited from an alcohol suspension in the form of a thin layer ($h \leq 100 \mu\text{m}$) on a heater substrate could be kept constant with an accuracy of $\leq 1\%$ or quickly (< 10 s) be changed using an electronic controller with the heater current (Delodovici *et al.*, 2017). Atomic oxygen with a flux density of up to $j_{\text{O}} = 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ was obtained by O_2 thermolysis according to the procedure (Brennan, 1967) on a current-heated rhodium (Rh) ribbon measuring $0.015 \times 1 \times 20$ mm.

A stream of CO molecules with a density of up to $j_{\text{CO}} \sim 2 \cdot 10^{20} \text{ cm}^{-2}\text{s}^{-1}$ could be introduced into a sample of $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ pre-purified by long-time (~ 2 hours) high-temperature ($T \sim 700$ K) heating in high vacuum ($\sim 10^{-8}$ Torr).

Free O atoms obtained by dissociation of O_2 on a ribbon (Rh) heated to 1800 K were previously adsorbed on the surface of $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ for 15 minutes from a mixture of $\text{O}_2 + \text{O}$ at an oxygen pressure of 0.02 Torr for 13 minutes at a sample temperature constant for all experiments (400 K and 2 minutes) when setting the operating temperature (379 K, 400 K, 550 K) (Achatz *et al.*, 2010; Lemmerer, 2020). Then the reaction volume with the sample was pumped out for 10 minutes to a vacuum of $3 \cdot 10^{-4}$ Torr and, further, a stream of CO was rapidly let in to a pressure of 0.5 Torr. The effect of triboluminescence, in this case, as shown by control experiments with nitrogen and inert gases, was negligible (Shang, 2017; Hsu *et al.*, 2017). During the filling process, the temperature of the sample was maintained by a constant high-speed electronic control system of the heater current. This made it possible to avoid side thermal effects (thermostimulated luminescence due to heat generation in the processes of adsorption and recombination, quenching of luminescence due to sample cooling during gas inlet, etc.) (Tanaka *et al.*, 2018; Bulychev, 2019; Bonacchi *et al.*, 2011; Hasobe, 2020). The flow of CO molecules onto the sample was supplied using a vacuum gate for a time $\Delta t < 1$ s to 90% of 0.5 Torr and then remained unchanged during continuous pumping (curves 6 and 3 in Figure 1 and Figure 2).

3. RESULTS AND DISCUSSION:

Figure 1 shows the luminescence kinetics in the activator (Mn^{2+} ion) emission band $\lambda_{\text{max}} = 527$ nm of the surface of α -willemite $\text{Zn}_{1.98}\text{Mn}_{0.02}\text{SiO}_4$ with pre-adsorbed O atoms that occurs when the stream of CO molecules is poured (Figure 1).

At the initial moment, the luminescence has the form of an adsorb luminescent (A.L.) flash (curves 1-5) (Accetta *et al.*, 2011; Sánchez-Carnerero *et al.*, 2015). At "low" sample temperatures ($T = 300$ K, 370 K, curves 1, 2), after the flare, the luminescence monotonically decreases according to the law characteristic of AL (Grankin *et al.*, 1981), in this case, the Eley-Rideal shock recombination process (Equation 2).

In Equation 2, L is the symbol of the adsorption center on the surface; $h\nu$ is the symbol of the emitted quantum of light. The luminescence decay kinetics is well described by the dependences of the form (Equation 3) at $T = 300$ K (curve 1) (Equation 4) at $T = 370$ K (curve

2). Here I is the luminescence intensity (relative units), t is time (seconds) (Babin *et al.*, 2015). At sample temperatures above 400 K, the second maximum begins to appear on the kinetic curve of luminescence decay, which is so pronounced at $T = 625$ K that it significantly exceeds the initial flash of luminosity and light sum (Figure 1, curve 5). Further luminescence decay after the second maximum occurs by law (Equation 5) at $T = 625$ K (Figure 1, curve 5) (which is characteristic of the second-order recombination process according to the Langmuir–Hinshelwood mechanism) (Zhu *et al.*, 2011; Kuznetsova and Rabinskiy, 2019). The second stage is possible only in the presence of adsorbed O-L atoms on the surface. Indeed, when CO is poured onto the same $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ sample, whose surface is filled only with molecular oxygen $\text{O}_2\text{-L}$, such luminescence curves with two maxima are not observed, and the intensity is almost two orders of magnitude lower than in the previous case (Figure 2).

In the opinion of the authors, the complex nature of the kinetic luminescence curves (Figure 1) may be due to the almost simultaneous occurrence of two types (stages) of the recombination process (Fahlman, 2018).

1. The stage of shock recombination (which is responsible for the initial flash) occurs non-activation. This is evidenced by the practical independence of the flash value on the sample temperature. The excitation of luminescence at this stage is most likely associated with the formation of electronically excited carbon dioxide molecules CO_2^e on the surface of solids (Bui and Dowell, 2020).

The formation of CO_2^e upon heterophasic oxidation of CO followed by radiative relaxation, is well known (Pravilov and Smirnova, 1981; Persson and Avouris, 1983). Figure 3 shows the dependence of the OC-O bond energy on the configuration coordinate (Pravilov and Smirnova, 1981). When the reagents come closer along the coordinate, the carbon dioxide molecule can enter the electronically excited states of CO_2^e ($^3\text{B}_2$, $^1\text{B}_2$).

It was shown in (Persson and Avouris, 1983) that even on the surface of metals, CO and CO_2 retain their individuality, in particular, the local structure of electronic terms remains almost unchanged (Pham *et al.*, 2016; Gupta, 2018). On the surface of crystallophosphorus (semiconductors, dielectrics) having a much lower density of electronic states, the formation of electronically excited states along the adiabatic

interaction path of (Equation 6) is much more likely (Figure 3). A further adsorbed electron-excited $\text{CO}_2^e\text{-L}$ molecule can radiatively relax to the ground state (Liu *et al.*, 2016). Luminescence in the blue and near-UV regions can be observed, slightly shifted to the short-wavelength region concerning homogeneous chemiluminescence with $\lambda_{\text{max}} \sim 430$ nm (Pravilov and Smirnova, 1981). On the surface of the crystallophosphorus-insulator, non-radiative energy transfer becomes possible from $\text{CO}_2^e(^3\text{B}_2)$ to the luminescence center (Mn^{2+} in our case) with the conservation of the total spin in the system (Equation 7) (Shigalugov *et al.*, 2000).

Since in the spectrum of this type of $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ luminescence (Figure 4) there is no (Equation 8) band with ~ 430 nm, it can be assumed that the transfer of electron excitation energy from the $\text{CO}_2^e(^3\text{B}_2)\text{-L}$ state to the surface and near-surface luminescence centers occurs at a rate significantly exceeding that of radiative relaxation ($10^5\text{--}10^7$ s $^{-1}$) in the (Equation 9) donor.

2. The second stage (with activation), responsible for the high-temperature maximum on the kinetic curve $I(t)$ (Figure 1, curves 3, 4 and 5), cannot be satisfactorily explained, like the source (Breysse *et al.*, 1978), only by surface recombination of adsorbed carbon monoxide molecules and oxygen atoms of the type (Equation 10).

This leads to a contradictory interpretation (process without and with activation) of different sections of the kinetic curves in Figure 1. The interpretation of this stage as the result of surface recombination of O-L atoms stimulated by the formed adsorption layer is most adequate (Liu and Qiu, 2015; Kumar and Srivastava, 2018). This layer consists, in this case, mainly of $\text{CO}_2\text{-L}$ molecules, due to the intense oxidation of CO molecules flying from the gas phase (Dhbaibi *et al.*, 2018). As accumulation on the surface of $\text{CO}_2\text{-L}$, at an elevated sample temperature ($T > 400$ K), the process of recombination of pre-adsorbed O-L atoms in the layer of $\text{CO}_2\text{-L}$ begins (Equation 11).

An increase in temperature is necessary here to accelerate the surface diffusion of O-L atoms with the participation of $\text{CO}_2\text{-L}$. This model corresponds to the quadratic in t of the regions of acceleration and decay of luminescence (Tsuchiya *et al.*, 2019; Hasobe, 2020). This is consistent with experience (second maxima in curves 4 and 5 of Figure 1). The band gap (about 6 eV) of the $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ sample significantly

exceeds the binding energy (5.18 eV) in the O₂ molecule (Chang *et al.*, 1999). The (O-O) bond has a small anharmonicity (12.2 cm⁻¹) and a small value of the vibrational quantum ($\eta\omega_o < 0.2$ eV). For these conditions, the adiabatic mechanism of luminescence excitation at this stage is most probable (Styrov *et al.*, 1989). The resulting adsorption complexes in the neutral (O-L + O-L) and charged (O-L + O⁻-L) forms can adiabatically enter electronically excited states $A^3\Sigma_u^+$, $c^1\Sigma_u^-$ for the neutral form O₂^e-L and $^4\Sigma_u^-$, $^2\Pi_u$, $^2\Sigma_u^-$ for the charged form (O₂⁻)^e-L (Rosen, 1970).

An effective non-radiative dipole transition with simultaneous energy transfer to luminescence centers located in the surface and near-surface regions is likely from the $^2\Pi_u$ term (Crassous, 2020; Tadashi, 2020). For example, the relaxation of an (O₂⁻)^e-L molecular ion to the ground state $X^2\Pi_g^1$ from the $^4\Sigma_u^-$, $^2\Pi_u$, $^2\Sigma_u^-$ states can occur in conjunction with the (Equation 12) transitions in the Mn²⁺ ion in Zn₂SiO₄:Mn²⁺ with the total spin remaining in the system. It is also possible to transfer energy to the centers of the activator and from neutral electronically excited (O₂)^e-L molecules (for example, upon transitions from (Equation 13) in the (O₂)^e-L molecule and (Equation 12) in the Mn²⁺ ion.

4. CONCLUSIONS:

Based on the experimental study carried out by spectral and kinetic methods, it was found that when a stream of carbon monoxide molecules is injected onto the surface of a solid – Zn₂SiO₄:Mn²⁺ crystallophosphorus with pre-adsorbed atomic oxygen, a luminescent glow appears in the characteristic activator emission band of the Mn²⁺ ion with a maximum near 527 nm, having a complex temporal nature. It was found that luminescence excitation proceeds in two main stages, somewhat time-shifted.

The first stage, which is responsible for the initial flare, proceeds non-activation according to the law characteristic of the shock recombination process. In this case, recombination of carbon monoxide molecules flying from the gas phase with oxygen atoms previously adsorbed on the surface of α-willemite appears according to the Eley–Rideal mechanism. In this case, the elementary mechanism of luminescence excitation includes the formation on the surface as a result of recombination of electronically excited carbon dioxide molecules, followed by non-radiative

transfer of excess energy to the Mn²⁺ luminescence centers.

The second stage has a pronounced activation character and begins to manifest itself only at temperatures above 400 K. The kinetics of the decay of luminescence at this stage obeys the law characteristic of the second-order recombination reaction. In this case, the luminescence excitation model in the acts of surface recombination of pre-adsorbed oxygen atoms according to the Langmuir–Hinshelwood mechanism stimulated by the formed adsorption layer of carbon dioxide molecules is most adequate to experiment. The excitation micromechanism of this model involves the formation on the surface of α-willemite of electronically excited molecular ions and neutral oxygen molecules from adiabatically recombining oxygen atoms in charged and neutral forms. Further, effective non-radiative dipole transitions in oxygen ions and molecules with simultaneous energy transfer to the Mn²⁺ luminescence centers located in the surface and near-surface regions while maintaining the full spin in the system become possible.

The proposed two-stage mechanism for the catalytic oxidation of carbon monoxide on the surface of α-willemite with pre-adsorbed atomic oxygen allows a consistent description of the luminescence observed in this case. This type of luminescence has the prospect of using for studying the mechanisms of catalytic oxidation of carbon monoxide, since using very sensitive informative optical methods allows revealing the details of the interaction of carbon monoxide with a crystalline catalyst containing atomic forms of oxygen in the surface layer, establishing the main stages of heterogeneous chemical reactions and studying patterns of atomic-molecular and electronic processes occurring on the surface.

5. REFERENCES:

1. Accetta, A., Corradini, R., and Marchelli, R. (2011). Enantioselective sensing by luminescence. In L. Prodi, M. Montalti, and N. Zaccheroni (Eds.), *Luminescence Applied in Sensor Science* (pp. 175-216). Berlin, Germany: Springer. doi:10.1007/978-3-642-19420-7
2. Achatz, D. E., Meier, R. J., Fischer, L. H., and Wolfbeis, O. S. (2010). Luminescent sensing of oxygen using a quenchable probe and upconverting nanoparticles. *Angewandte*

Chemie International Edition, 50(1), 260-263.
doi:10.1002/anie.201004902

3. Achatz, D. E., Reham, A., and Wolfbeis, O. S. (2011). Luminescent chemical sensing, biosensing, and screening using upconverting nanoparticles. In L. Prodi, M. Montalti, and N. Zaccheroni (Eds.), *Luminescence Applied in Sensor Science* (pp. 29-50). Berlin, Germany: Springer. doi:10.1007/128_2010_98
4. Arnold, G. S., and Coleman, D. J. (1988). Surface mediated radical recombination luminescence: O+NO+Ni. *Journal of Chemical Physics*, 88(11), 7147-7156.
5. Babin, V., Chernenko, K., Lipińska, L., Mihokova, E., Nikl, M., Schulman, L.S., Shalapska, T., Suchocki, A., Zazubovich, S., Zhydachevskii, Ya. (2015). Luminescence and excited state dynamics of Bi³⁺ centers in Y₂O₃. *Journal of Luminescence*, 167, 268-277. doi:10.1016/j.jlumin.2015.06.029
6. Barashkin, R. L., and Samarin, I. V. (2005). Computer system of simulating operating duty of a gaslifting well. In *11th International Scientific and Practical Conference of Students, Postgraduates and Young Scientists; "Modern Techniques and Technologies", MTT 2005 – Proceedings*. Retrived from <https://ieeexplore.ieee.org/document/4493238>
7. Bonacchi, S., Genovese, D., Juris, R., Montalti, M., Prodi, L., and Rampazzo, E. (2011). Luminescent chemosensors based on silica nanoparticles. In L. Prodi, M. Montalti, and N. Zaccheroni (Eds.), *Luminescence Applied in Sensor Science* (pp. 93-138). Berlin, Germany: Springer. doi:10.1007/978-3-642-19420-7
8. Brennan, D. (1967). Atomization of diatomic molecules on metals. In *Catalysis. Physical and Chemistry of Heterogeneous Catalysis* (pp. 288-317). Moscow, Russian Federation: Mir.
9. Breyse, M., Claydel, B., Faure, L., and Guenin, M. (1978). Chemiluminescence induced by catalysis. *Reviews of Chemical Intermediates*, 2, 75-103.
10. Bui, M., and Dowell, N.M. (2020). *Carbon capture and storage*. Cambridge, United Kingdom: Royal Society of Chemistry.
11. Bulychev, N. A. (2019). On the hydrogen production during the discharge in a two-phase vapor-liquid flow. *Bulletin of the Lebedev Physics Institute*, 46(7), 219-221.
12. Chang, H., Park, H. D., Sohn, K. S., and Lee, J.D. (1999). Electronic Structure of Zn₂SiO₄ and Zn₂SiO₄: Mn. *Journal of the Korean Physical Society*, 34, 545–548.
13. Crassous, J. (2020). Circularly polarized luminescence in Helicene and Helicenoid derivatives. In *Circularly Polarized Luminescence of Isolated Small Organic Molecules* (pp. 53-97). Retrived from <https://www.springer.com/gp/book/9789811523083>. doi:10.1007/978-981-15-2309-0
14. Delodovici, F., Manini, N., Wittman, R.S., Choi, D.S., Fahim, M.A., and Burchfield, L.A. (2017). Protomene: A new carbon allotrope. *Carbon*, 126, 574-579. doi:10.1016/j.carbon.2017.10.069
15. Dhbaibi, K., Favereau, L., Srebro, M., Jean, M., Vanthuyne, N., Zinna, F., Jamoussi, B., Di Bari, L., Autschbach, J., and Crassous, J. (2018). Exciton coupling in diketopyrrolopyrrole-helicene derivatives leads to red and near-infrared circularly polarized luminescence. *Chemical Science*, 9, 535-778. doi:10.1039/C7SC04312K
16. Dove, D. B., Takamori, T., Chang, I. F., Thioulouse, P., Mendez, E.E., and Giess, E.A. (1981). Influence of electron trap on the phosphorescence of Zinc silicate mn phosphors. *Journal of Luminescence*, 24, 317–320.
17. Fahlman, B. D. (2018). *Materials chemistry*. Retrived from <https://link.springer.com/book/10.1007/978-94-007-0693-4>
18. Formalev, V. F., Kolesnik, S. A., and Kuznetsova, E. L. (2018). Wave heat transfer in the orthotropic half-space under the action of a nonstationary point source of thermal energy. *High Temperature*, 56(5), 727-731.
19. Formalev, V. F., Kolesnik, S. A., and Kuznetsova, E. L. (2019). Effect of components of the thermal conductivity tensor of heat-protection material on the value of heat fluxes from the gasdynamic boundary layer. *High Temperature*, 57(1), 58-62.
20. Grankin, V. P., Nikolaev, I. A., Styrov, V. V., and Tyurin, Yu. I. (1981).

- Adsorboluminescence of crystals in molecular oxygen beams. *Theoretical and Experimental Chemistry*, 17(6), 757–773.
21. Gupta, T. (2018). *Carbon The Black, the Gray and the Transparent Authors*. Berlin, Germany: Springer International Publishing. doi:10.1007/978-3-319-66405-7
 22. Hasobe, T. (2020). Structural control of fluorescent helicates for improved circularly polarized luminescence properties. In T. Mori (Ed.), *Circularly polarized luminescence of isolated small organic molecules* (pp. 99–116). Singapore, Singapore: Springer Nature. doi:10.1007/978-981-15-2309-0
 23. Hess, H., and Krautz, E. (1981). Photoluminescence and photoconductivity of undoped and doped zinc silicate. *Journal of Luminescence*, 24, 321–324.
 24. Hsu, C.-P., Hejazi, Z., Armagan, E., Zhao, S., Schmid, M., Zhang, H., Guo, H., Weidenbacher, L., Rossi, R.M., Koebel, M.M., Boesel, L.F., and Toncelli, C. (2017). Carbon dots and fluorescein: The ideal FRET pair for the fabrication of a precise and fully reversible ammonia sensor. *Sensors and Actuators B: Chemical*, 253, 714–722. doi:10.1016/j.snb.2017.07.001
 25. Juanjuan, P., Teoh, C. L., Zeng X., Samanta A., Wang, L., Xu, W., Su, D., Yuan, L., Liu, X., and Chang, Y.-T. (2015). Development of a highly selective, sensitive, and fast response upconversion luminescent platform for hydrogen sulfide detection. *Advanced Functional Materials*, 26(2), 191–199. doi:10.1002/adfm.201503715
 26. Kharisov, B. I., and Kharissova, O. V. (2019). General data on carbon allotropes. In *Carbon allotropes: Metal-complex chemistry, properties and applications* (pp. 1–8). Cham, Switzerland: Springer.
 27. Koshoridze, S. I., Levin, Y. K., Rabinskiy, L. N., and Babaytsev, A. V. (2017). Investigation of deposits in channels of panels of a heat-transfer agent. *Russian Metallurgy (Metally)*, 2017(13), 1194–1201.
 28. Kumar, N., and Srivastava, V.C. (2018). Simple synthesis of large graphene oxide sheets via electrochemical method coupled with oxidation process. *ACS Omega*, 3(8), 10233–10242. doi:10.1021/acsomega.8b01283
 29. Kuznetsova, E. L., and Rabinskiy, L. N. (2019). Heat transfer in nonlinear anisotropic growing bodies based on analytical solution. *Asia Life Sciences*, 2, 837–846.
 30. Lemmerer, M. (2020). *Chemoselective nucleophilic α -amination of amides*. Wiesbaden, Germany: Springer Fachmedien Wiesbaden. doi:10.1007/978-3-658-30020-3
 31. Liu, X., and Qiu, J. (2015). Recent advances in energy transfer in bulk and nanoscale luminescent materials: from spectroscopy to applications. *Chemical Society Reviews*, 44(23), 8714–8746. doi:10.1039/C5CS00067J
 32. Liu, Y., Cerezo, J., Mazzeo, G., Lin, N., Zhao, X., Longhi, G., Abbate, S. and Santoro, F. (2016). Vibronic coupling explains the different shape of electronic circular dichroism and of circularly polarized luminescence spectra of hexahelicenes. *Journal of Chemical Theory and Computation*, 12, 2799–2819.
 33. Lurie, S. A., Solyaev, Y. O., Lizunova, D. V., Rabinskiy, L. N., Bouznik, V. M., and Menshykov, O. (2017). Influence of mean distance between fibers on the effective gas thermal conductivity in highly porous fibrous materials. *International Journal of Heat and Mass Transfer*, 109, 511–519.
 34. Ni, F., Zhu, Z., Tong, X., Xie, M., Zhao, Q., Zhong, C., Zou, Y., and Yang, C. (2018). Organic emitter integrating aggregation-induced delayed fluorescence and room-temperature phosphorescence characteristics, and its application in time-resolved luminescence imaging. *Chemical Science*, 9, 6150–6155. doi:10.1039/C8SC01485J 1970.
 35. Palumbo, D. T., and Brown, J. J. (1970). Electronic States of Mn²⁺-Activated Phosphors. *Journal of the Electrochemical Society*, 117, 1184–118.
 36. Persson, B. N., and Avouris, Ph. (1983). On the nature and decay electronically exited states at metal surfaces. *Journal of Chemical Physics*, 79(10), 5156–5162.
 37. Pham, T. N., Ono, S., and Ohno, K. (2016). Ab initio molecular dynamics simulation study of successive hydrogenation reactions of carbon monoxide producing methanol. *Journal of Chemical Physics*, 144, article number 144309. doi:10.1063/1.4945628

38. Pravilov, A. M., and Smirnova, L. G. (1981). Chemiluminescence processes in the $O(3P) + CO + M$ system. Isolation of the heterogeneous component of reactions involving impurities. *Kinetic and Catalysis*, 22(3), 559-563.
39. Radyuk, A. G., Gorbatyuk, S. M., Tarasov, Y. S., Titlyanov, A. E., and Aleksakhin, A. V. (2019). Improvements to mixing of natural gas and hot-air blast in the air tuyeres of blast furnaces with thermal insulation of the blast duct. *Metallurgist*, 63(5-6), 433-440.
40. Rivera-Enríquez, C. E., Fernandez-Osorio, A., and Chavez-Fernandez, J. (1981). Luminescence properties of a- and b- $Zn_2SiO_4:Mn$ nanoparticles prepared by a co precipitation method. *Journal of Alloys and Compounds*, 688, 775–782.
41. Rosen, B. (Ed). (1970). *Spectroscopic data relative to diatomic molecules*. Oxford, United Kingdom: Pergamon Press.
42. Rufov, Yu. N., Kadushin, A. A., and Roginsky S. Z. (1966). The emergence of luminescence during the adsorption of vapors and gases on solids. *Doklady AN SSSR*, 171(4), 905-906.
43. Sánchez-Carnerero, E. M., Agarrabeitia, A. R., Moreno, F., Maroto, B. L., Muller, G., Ortiz, M. J., and de la Moya, S. (2015). Circularly polarized luminescence from simple organic molecules. *Chemistry Europe*, 21(39), 13488-13500. doi:10.1002/chem.201501178
44. Sarrigani, G. V., and Amiri, I. S. (2019). Willemite-based glass ceramic doped by different percentage of erbium oxide and sintered in temperature of 500-1100C. In *Physical and optical properties* (pp.65-66). Cham, Switzerland: Springer. doi:10.1007/978-3-030-10644-7
45. Shang, R. (2017). *New carbon-carbon coupling reactions based on decarboxylation and iron-catalyzed C-H activation*. Singapore, Singapore: Springer. doi:10.1007/978-981-10-3193-9
46. Shigalugov, S. H., Tyurin, Y. I., Borovitskaya, A. O., and Dubrov D. V. (2019). Experimental installation phosphors luminescence excitation, stimulation and extinguishing by atomic and molecular beams. *Periodico Tchê Química*, 16 (31), 809-815.
47. Shigalugov, S. Kh., Tyurin, Yu. I., Styrov, V. V., and Tolmacheva, N. D. (2000). Heterogeneous chemiluminescence of crystallophosphorus catalysts in a $CO + O$ mixture. *Kinetics and Catalysis*, 41(4), 566-592.
48. Skvortsov, A. A., Kalenkov, S. G., and Koryachko, M. V. (2014). Phase transformations in metallization systems under conditions of nonstationary thermal action. *Technical Physics Letters*, 40(9), 787-790.
49. Stevels, A. L. N., and Vink, A. T. (1974). Fine Structure in the low temperature luminescence of $Zn_2SiO_4:Mn$ and $Mg_4Ta_2O_9:Mn$. *Journal of Luminescence*, 8, 443-451.
50. Styrov, V. V., Tyurin, Yu. I., and Shigalugov, S. X. (1989). Luminescence of crystalline phosphors in atomic oxygen, P. Excitation mechanisms. *Kinetics and Catalysis*, 30(2), 389—395.
51. Tadashi, M. (2020). Frontiers of circularly polarized luminescence chemistry of isolated small organic molecules. In M. Tadashi (Ed.), *Circularly polarized luminescence of isolated small organic molecules* (pp. 1-10). Singapore, Singapore: Springer.
52. Tanaka, H., Inoue, Y. and Mori, T. (2018). Circularly polarized luminescence and circular dichroism in small organic molecules: correlation between excitation and emission dissymmetry factors. *ChemPhotoChem*, 2, 386-402.
53. Tsuchiya, Y., Ikesue, K., Nakanotani, H., and Adachi, C. (2019). Photostable and highly emissive glassy organic dots exhibiting thermally activated delayed fluorescence. *Chemical Communications*, 55, 5215-5218. doi:10.1039/C9CC01420A
54. Volkenstein, F. F., Gorban, A. N., and Sokolov, V. A. (1976). *Radical recombination luminescence of semiconductors*. Moscow, Russian Federation: Nauka.
55. Zhou, J., Liu, Q., Feng, W., Sun, Y., and Li, F. (2015). Upconversion luminescent materials: Advances and applications. *Chemical Reviews*, 115(1), 395-465.
56. Zhu, S., Fischer, T., Wan, W., Descalzo, A. B., and Rurack, K. (2011). Luminescence amplification strategies integrated with microparticle and nanoparticle platforms. In

L. Prodi, M. Montalti, and N. Zaccheroni (Eds.), *Luminescence applied in sensor science* (pp. 51-91). Berlin, Germany: Springer.

$$\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2 \quad (\text{Eq. 1})$$

$$\text{CO} + \text{O-L} \rightarrow \text{CO}_2\text{-L} + (h\nu). \quad (\text{Eq. 2})$$

$$I(t) = \frac{35}{t}(1 - e^{-1.2t}), \quad (\text{Eq. 3})$$

$$I(t) = \frac{123}{t}(e^{-0.02t} - e^{-0.473t}) \quad (\text{Eq. 4})$$

$$I(t) = 3 \cdot 10^3 / (1 + 1.1t)^2 \quad (\text{Eq. 5})$$

Figure 1. Luminescence flashes of α -willemite ($\lambda_{\max} = 527 \text{ nm}$) upon admission of a flow of CO molecules ($j_{\text{CO}} = 1.9 \cdot 10^{20} \text{ cm}^{-2} \cdot \text{s}^{-1}$) onto the surface of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ with pre-adsorbed O-L atoms. Sample temperature 300 K (1), 370 K (2), 400 K (3), 550 K (4) ad 625 K (5). O atoms obtained thermolytically (by dissociation of O_2 on an Rh tape) were preliminarily adsorbed by α -willemite for 15 minutes at $p_{\text{O}+\text{O}_2} = 0.02 \text{ Torr}$ and $T = 295 \text{ K}$; 6 – kinetics of establishing the pressure of CO in the chamber. Source: the author

Figure 2. Luminescence flashes of α -willemite ($\lambda_{\max} = 527 \text{ nm}$) upon the inlet of a flow of CO molecules ($j_{\text{CO}} = 1.9 \cdot 10^{20} \text{ cm}^{-2} \cdot \text{s}^{-1}$) onto the surface of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ pre-filled with O_2 -L molecules (pre-adsorption of O_2 15 minutes at $p_{\text{O}_2} = 0.02 \text{ Torr}$ and $T = 295 \text{ K}$). Sample temperature 400 K (1) and 550 K (2); 3- kinetics of establishing the pressure of CO in the chamber. Source: the author

Figure 3. The dependence of the binding energy (OC-O) on the configuration coordinate r . Source: according to Pravilov and Smirnova (1981)

Figure 4. The spectrum of photoluminescence (1) and chemiluminescence (2) of α -willemite $\text{Zn}_{1.98}\text{Mn}_{0.02}\text{SiO}_4$ at $T = 625 \text{ K}$. Source: the author